The Ohio State University

Optimization of Palladium Promoted Transition Metal Catalysts for Lean Methane Oxidation

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Introduction

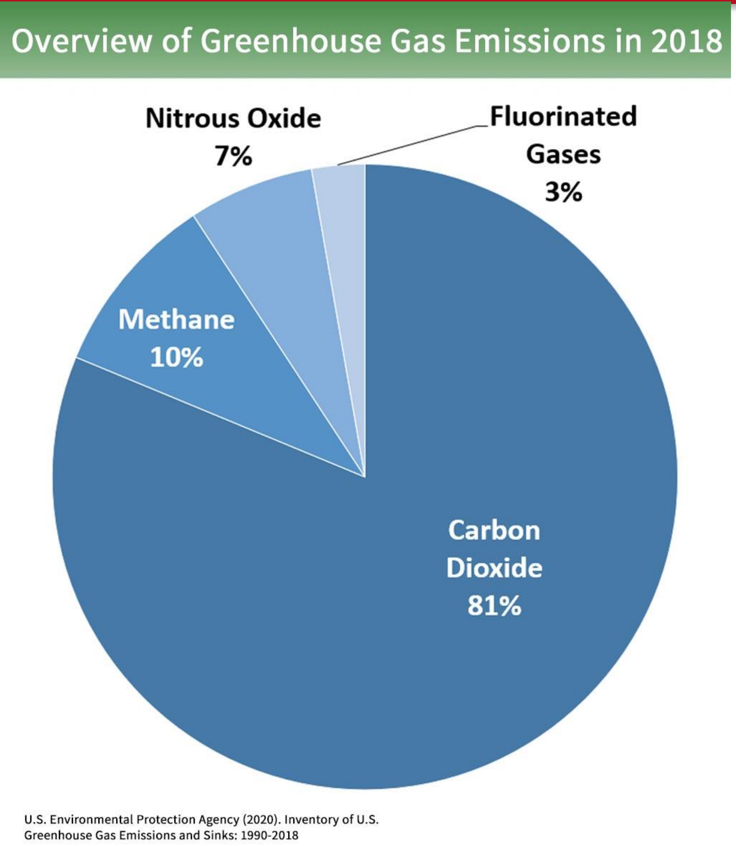

Figure 1: Major greenhouse gases [1]

Motivation: Greenhouse Gases

- CO_2 appears to have the highest contribution to the global warming
- However, methane (CH_4) global warming potential (GWP) is 25 times that of CO_2 [2]
- Coal mining represents almost 10% of the United States methane emissions

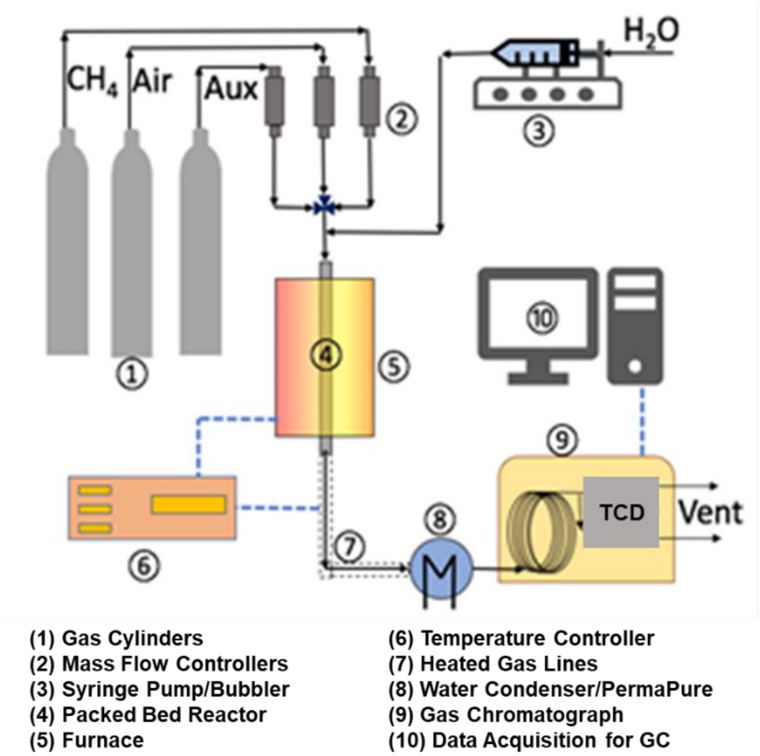

Figure 2: Catalytic activity test system [3]

Background: Methane Mitigation

- Ventilation systems ensure the safety of workers, but ventilation air methane (VAM) is released to the atmosphere
- Two approaches to VAM mitigation:
  - Ancillary
  - Principal
- Catalytic flow reversal reactor
  - Lower operating temperatures
  - Eliminating NO_x emission

Background: Catalyst Selection

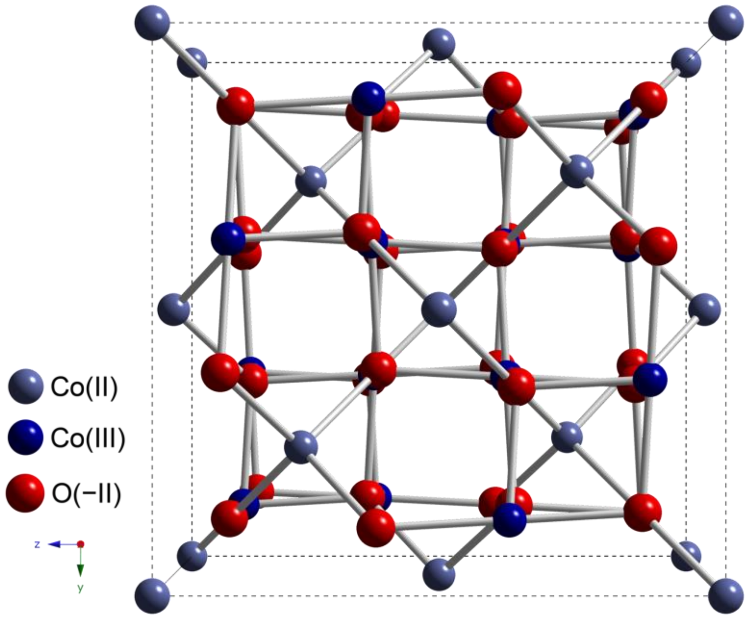

Figure 3: Unit cell of Co_3O_4 [6]

- Noble metals typically used due to high activity
- Palladium (Pd) and Platinum (Pt) for methane oxidation
  - Pd can form highly active PdO [5]
- Downsides to noble metals
  - High cost
  - Scarcity
  - Sensitivity to water
- Transition metals as alternatives
  - Cobalt (II,III) oxide: Co_3O_4

Methods

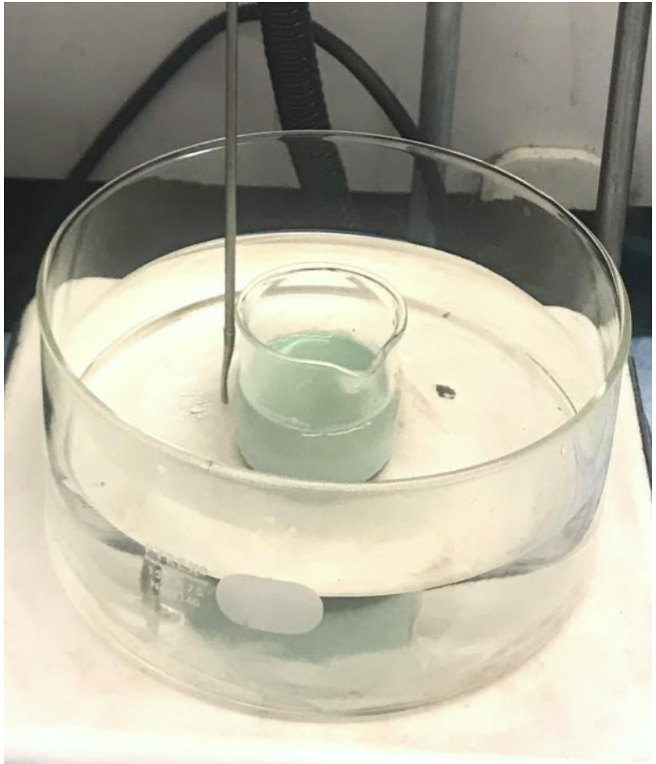

Figure 4: Wet impregnation mixture

Catalyst Synthesis

- Wetness impregnation (WI) technique
- Cobalt on metal oxide support materials
    - alumina (Al_2O_3), silica (SiO_2), zirconia (ZrO_2) and ceria (CeO_2)
- Solvent evaporation and dried in oven
- Calcined with air at 400°C for 3 hours

Figure 5: X-ray diffraction instrument

Catalyst Characterization

- X-ray diffraction (XRD) technique
- Detects intensity of scattered x-rays
- Characteristic peaks for each compound
- Bragg's Law:

$$n\,\lambda = 2\,d\,sin(\theta)$$

Temperature programmed reduction

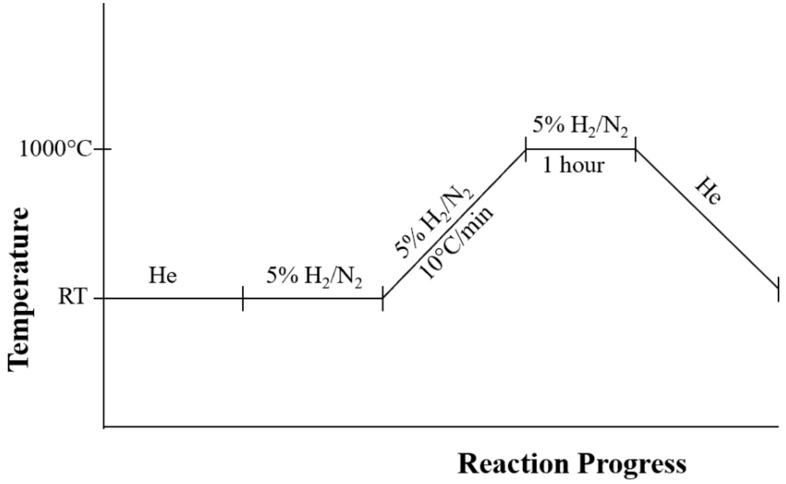

Figure 6: TPR Heating Scheme

- Reducibility of the Co_3O_4 active sites
- Oxygen mobility of catalysts
- 5% hydrogen in nitrogen
- 1000°C for 1 hour
- Gas outlet to mass spectrometer

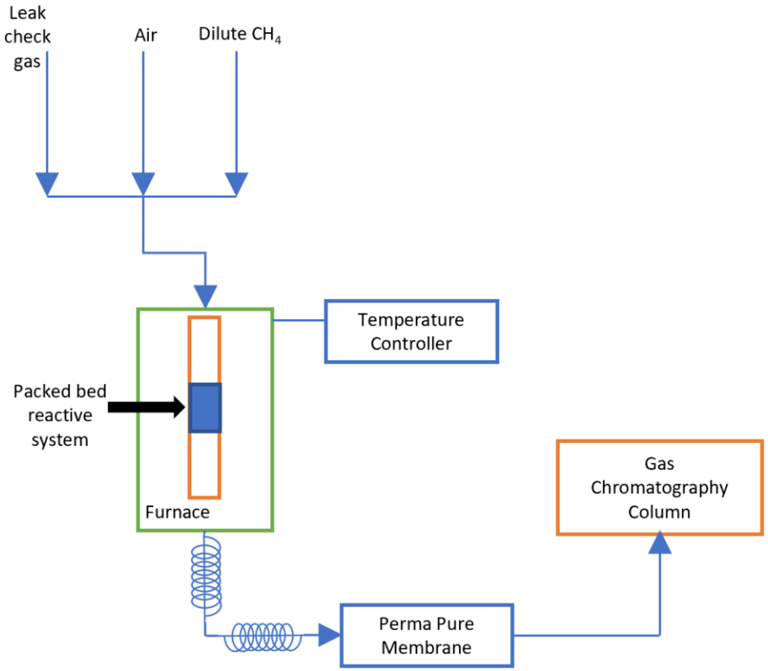

Figure 7: Activity Test Setup

Activity Tests

- Packed bed reactor system
  - 50mg of catalyst, bed height of 0.4cm
- Activity screening to find best catalyst
- Methane conversion tests
  - Promoter comparison
  - Water stability

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Results

XRD Catalyst Characterization

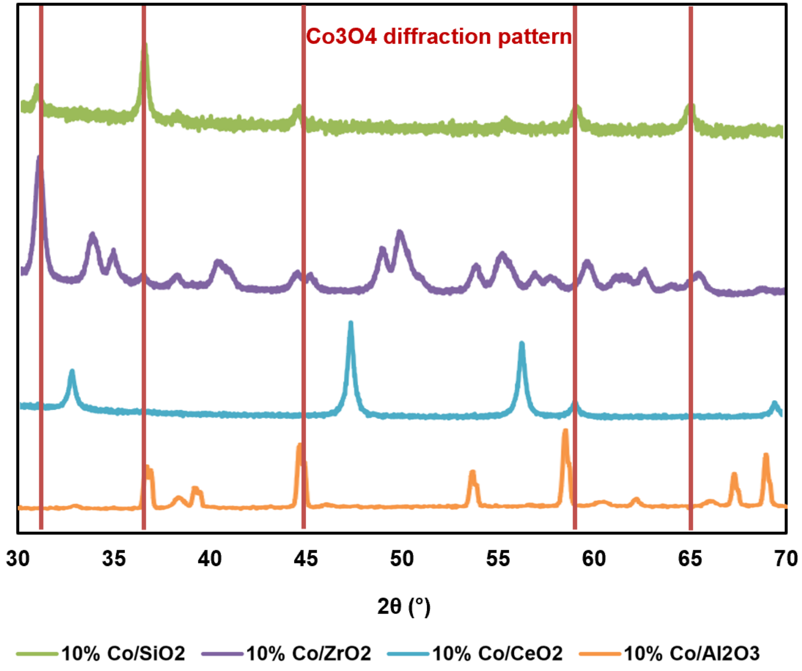


Figure 8: XRD Patterns

- Investigate crystalline structures
- Diffraction pattern of synthesized catalysts
- Red bars show Co_3O_4 diffraction pattern [4]
- Indicates that Co has been oxidized to Co_3O_4 during calcination

Activity Tests

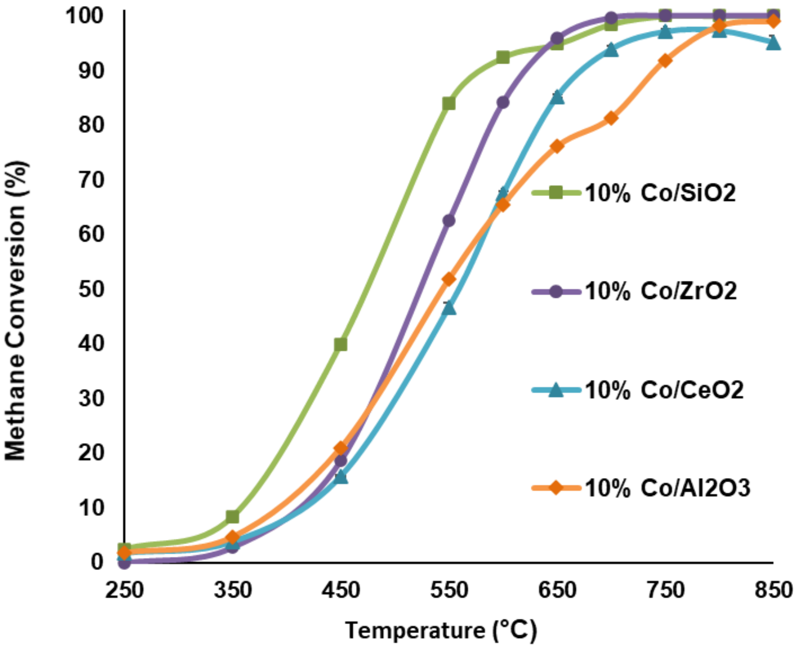


Figure 9: Lean methane oxidation activity

- 10% Co/SiO_2 better at lower temperatures
- At higher temperatures, 10% Co/ZrO_2 and 10% Co/SiO2 had similar activity
- Unexpected high activity of 10% Co/SiO_2
  - High surface area (~300 m^2/g)
  - Lower GHSV (gas hourly space velocity) value due to lower density

Temperature programmed reduction (TPR)

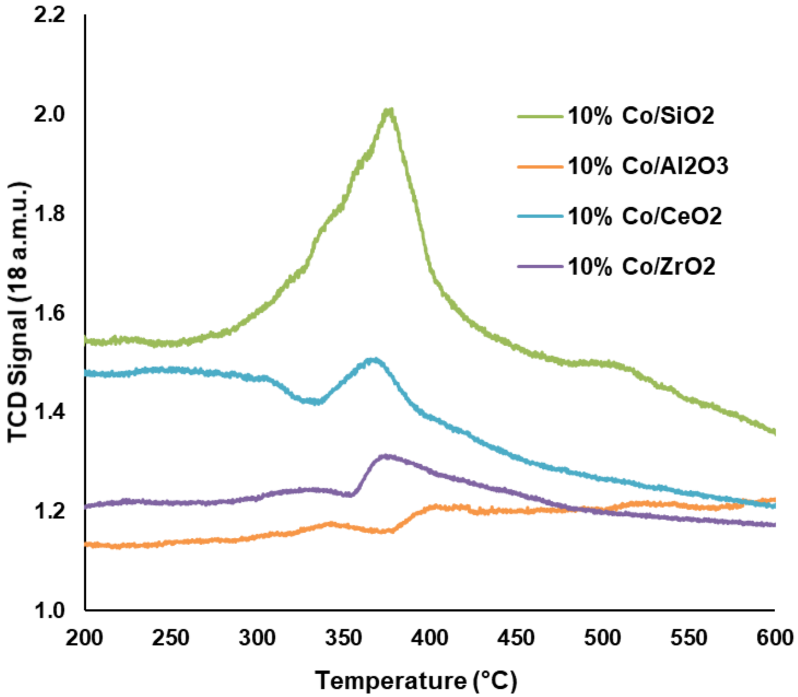
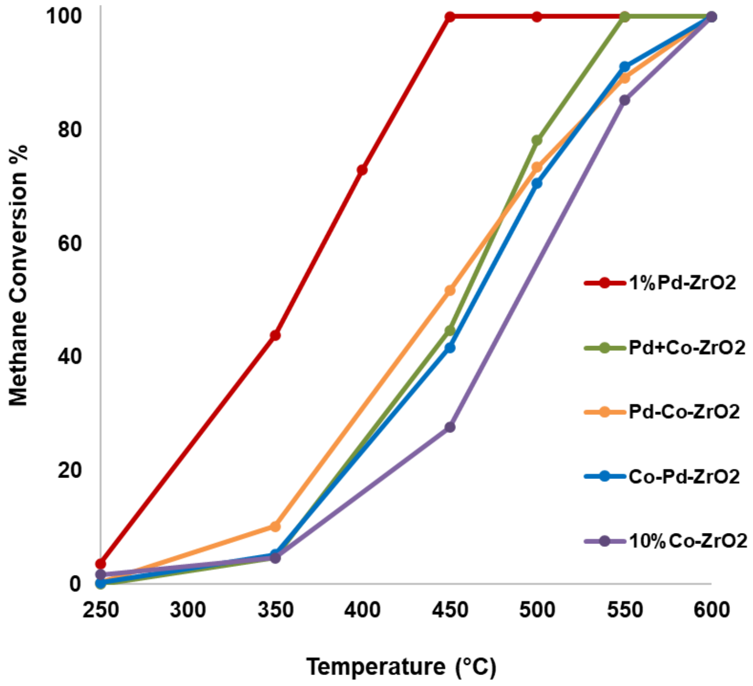


Figure 10: TPR of 10% Co/SiO_2, Al_2O_3, CeO_2, and ZrO_2

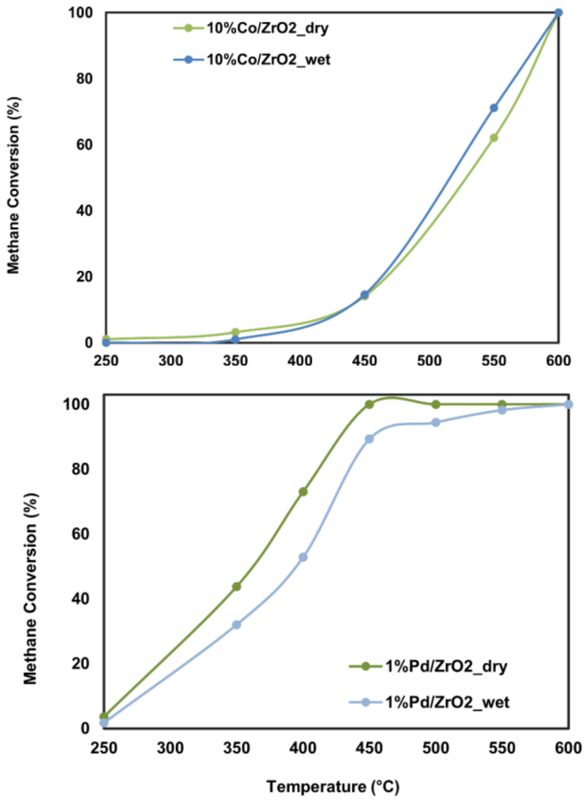
- Thermal conductivity detector (TCD)
- Reducibility of Co_3O_4 on different support materials
- Areas under curves:
  - 10% Co/SiO_2 >> 10% Co/ZrO_2
- Co_3O_4 phase reduced to CoO and Co:
  - Greatest in 10% Co/SiO_2
  - Least in 10% Co/ZrO_2
- 10% Co/ZrO_2 chosen due to activity and resistance to reduction of Co_3O_4 phase

Promoter Addition



- Palladium as promoter, Pd/PdO active phase
- Comparison of promoter and order of synthesis
- 3 varied orders showed differences due to accessibility of Pd on catalyst surface
- Pd-Co-ZrO_2 was deactivated at higher temperatures due to H_2O

Figure 11: TPR of 10% Co/SiO_2, Al_2O_3, CeO_2, and ZrO_2



Wet Activity Tests of Co and Pd Catalysts

- Catalytic activity test with 3% water in the feed
- Cobalt catalyst not affected
- Palladium catalyst showed inhibition with water
- Pd activity higher overall, but Co preferred because no deactivation

Figure 12: Activity tests in the presence and absence of water

Long-Term Stability Test: Pd

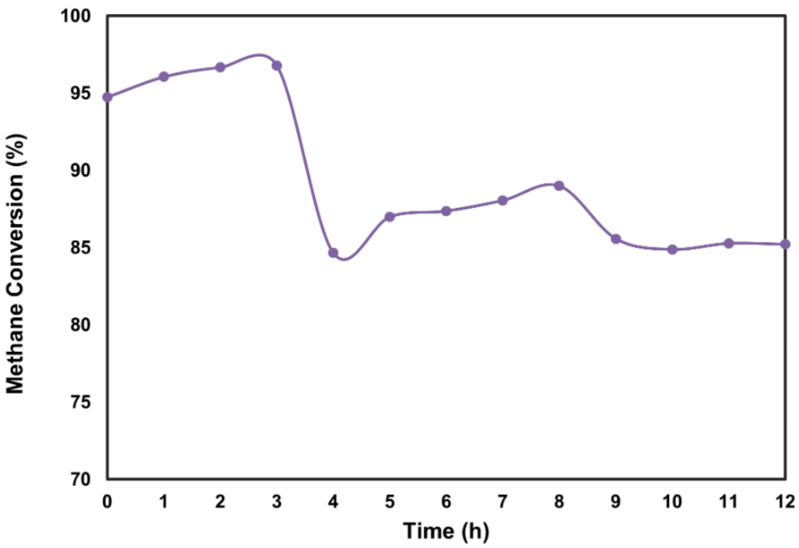


Figure 13: Wet methane oxidation of 10% Co/ZrO2

- Testing 1% Pd/ZrO_2 catalyst
  - In presence of 3% water
- Showed instability of palladium catalyst over time in presence of water
  - Over the long-term test
- Not recommended as catalyst deactivates

Long-Term Stability Test: Co

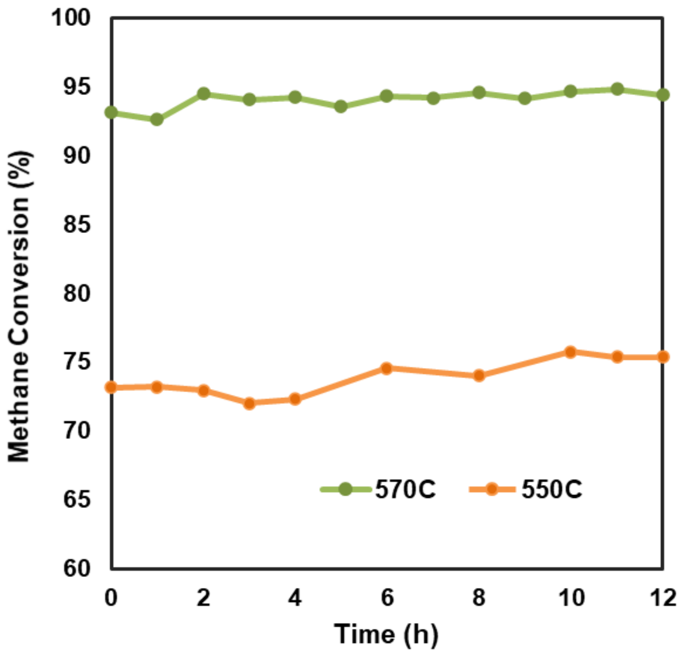
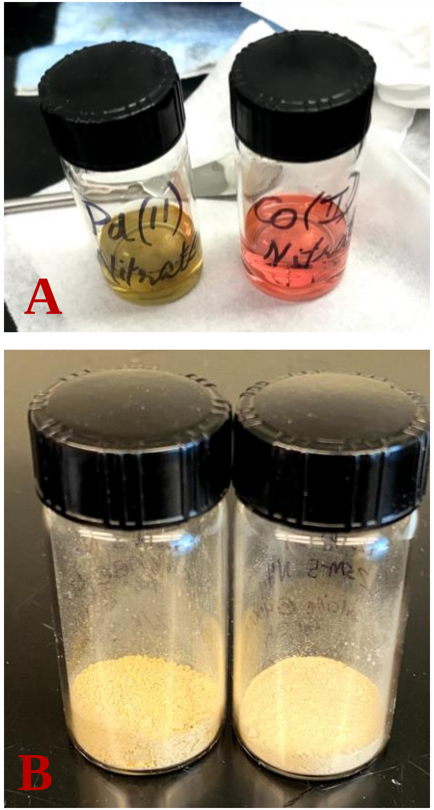


Figure 14: Wet methane oxidation of 10% Co/ZrO2

- Testing the 10% Co/ZrO_2 catalyst in the presence of water
- Activity test performed at 550°C and 570°C for 12 h
- Showed that the Co/ZrO_2 catalyst is highly stable catalyst under reaction conditions:
  - Operated at two different methane conversion conditions
  - Resistant to presence of water

Conclusion

Conclusion



Summary

- Catalytic mitigation of coal-mine VAM
- Cobalt catalysts synthesized on different metal oxide supports
- Pd promotion showed similar to Pd based
- Co-based showed resistance to presence of water vapor
- Demonstrated the potential Co/ZrO_2 catalyst
- Co-based more economically feasible than Pd-based

Figure 15: Catalysts at the A. beginning and B. end of synthesis

Future Work

Future Work

Commercialization

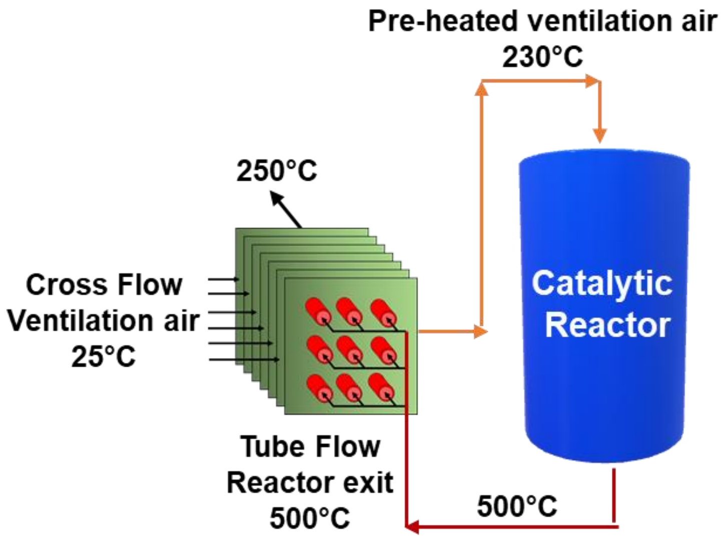


Figure 16: Commercial Design for Catalytic Oxidation of VAM [3]

- Catalytic oxidation reduces the auto-ignition temperature and NO_x emission
- Balances on system show exhaust stream can be used for pre-heating
- Further pilot-scale research needed:
    - Fluctuations in pressure and temperature
    - Verify scaled-up parameters
    - Effect on NO_x emission

References

[1] *Overview of Greenhouse Gases*. 8 Sept. 2020, www.epa.gov/ghgemissions/overview-greenhouse-gases.

[2] Forster, P., V. Ramaswamy, P. Artaxo, T. Berntsen, R. Betts, D. Fahey, J. Haywood, J. Lean, D. Lowe, G. Myhre, J. Nganga, R. Prinn, G. Raga, M. Schulz & R. Van Dorland (2008): Changes in Atmospheric Constituents and in Radiative Forcing. Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the IPCC, S. Solomon et al. (eds.), Cambridge University Press, Cambridge, UK, Chapter 2 http://www.cambridge.org/catalogue/catalogue.asp?isbn=9780521705967

[3] Ozkan, U., S. Gunduz, D. Jain, B. Wynne. "Catalytic Combustion of Methane Emitted from Coal Mine Ventilation Air Systems." OCRC Agreement Number: R-17-14.

[4] Kumari, T. Sri Devi, T. Prem Kumar, and A. Manuel Stephan. "Lithium insertion behavior of nanoscopic Co3O4 prepared with avian egg membrane as a template." Bull. Korean Chem. Soc 32.4 (2011): 1205.

[5] Baldwin, T. R., and R. Burch. "Catalytic combustion of methane over supported palladium catalysts: I. Alumina supported catalysts." Applied catalysis 66.1 (1990): 337-358.

[6] Mills, B. Ball-and-stick model of the unit cell of cobalt(II,III) oxide, Co3O4. Colour code: Cobalt(II), CoII: lighter blue Cobalt(III), CoIII: darker blue Oxygen, O: red Crystal structure from J. Magn. Magn. Mater. (2006) 300, 300–305 Image generated in CrystalMaker 8.2.

Questions?

Recap:

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